

#23/gm  
02.25.03

## VERIFICATION OF A TRANSLATION

I, the below named translator, hereby declare that:

My name and post office address are as stated below:

That I am knowledgeable in the English language and in the language in which the below identified Japanese application was filed, and that I believe that the English translation of the Japanese patent application No. 10(1998)-278023 filed on September 30, 1998 attached hereto is a true and complete translation of the above-identified Japanese application as filed.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date

January 31, 2003

Full name of the translator

Ohno Kiwam

RECEIVED  
FEB 13 2003  
TC 1700

Signature of the translator

Ohno Kiwam

Post Office Address

c/o Yanagawa & Company  
Mitsuya-Yotsuya Building, 8th Floor,  
2-14, Yotsuya, Shinjuku-ku, Tokyo,  
160-0004 Japan



10-278023  
Name of Documents: Patent Application  
Docket Number: P-30283  
Date of Filing: September 30, 1998  
To: Director of the Patent Office, Esq.  
IPC.: C09D 11/00  
B41M 5/00  
Title of the Invention: Ink for inkjet and inkjet recording method  
Inventor(s)  
Address: c/o Fuji Photo Film Co., Ltd., No. 210, Nakanuma, Minami-ashigara-shi, Kanagawa, 250-0123 Japan  
Name: Makoto Yamada  
Toshiki Fujiwara  
Applicant(s)  
Registration Number: 000005201  
Name: FUJI PHOTO FILM CO., LTD..  
Agent:  
Registration Number: 100073874  
Patent Attorney  
Name: Taira Hagino  
Telephone Number 03-5561-3990  
Agent:  
Registration Number: 100066429  
Patent Attorney  
Name: Toshio Fukazawa  
Telephone Number 03-5561-3990  
Agent:  
Registration Number: 100093573  
Patent Attorney  
Name: Zenichi Soeda  
Telephone Number 03-5561-3990  
Agent:  
Registration Number: 100105474  
Patent Attorney  
Name: Hironori Honda  
Telephone Number 03-5561-3990  
Agent:  
Registration Number: 100090343  
Patent Attorney  
Name: Yuriko Kuriu  
Telephone Number 03-5561-3990  
List of the Filed Material  
Name of the Material: Specification one (1)  
Abstract one (1)  
Number of General Authorization: 9723355

RECEIVED  
FEB 13 2003  
TC 1700



- 1 -

[Name of document] Specification

[Title of invention] Jet printing ink and ink-jet recording method

5

[Scope of claims]

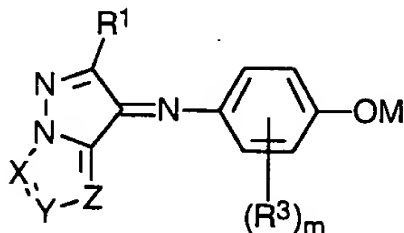
[Claim 1] A jet printing ink comprising a dye and an aqueous medium, which further comprises a polymer having a tertiary amino group or a nitrogen atom-containing hetero-  
10 cyclic group.

[Claim 2] The jet printing ink of claim 1, wherein the polymer has a quaternary cationic group as the tertiary amino group or the nitrogen atom-containing heterocyclic  
15 group.

[Claim 3] The jet printing ink of claim 1 or 2, wherein the dye is a compound represented by the formula 1 to 4.

20

Formula 1



RECEIVED

FEB 13 2003

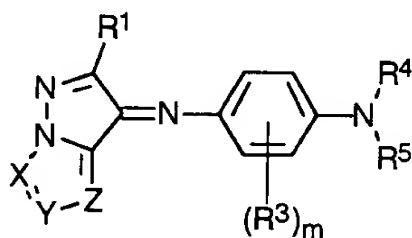
TC 1700

In the formula, each of R<sup>1</sup> and R<sup>3</sup> independently is a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, cyano, amido,  
25 sulfonamido, ureido, an alkoxycarbonylamino group, an alkylthio group, an arylthio group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an acyl group, an amino group, or an alkylamino group. (A benzene ring contained in the substituent group can further

have a substituent group selected from the group consisting of a halogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, cyano, amido, sulfonamido, ureido, an alkoxycarbonylamino group, an alkylthio group, an arylthio group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an acyl group, an amino group and an alkylamino group).  $m$  is an integer of 0 to 4. In the case  $m$  is 2 to 4, the groups of  $R^3$  can be different from each other.

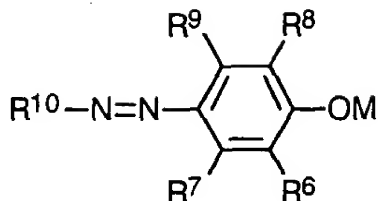
Each of  $X$ ,  $Y$  and  $Z$  independently is  $=N-$  or  $=CR^2-$ , in which  $R^2$  is a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, a heterocyclic group, an alkoxy group, or an aryloxy group; in the case that both of  $X$  and  $Y$  are  $=CR^2-$ , these two  $R^2$  can be combined to form a ring; and  $M$  is a hydrogen atom, a dissociated inorganic base, a primary amine, a secondary amine, or a tertiary amine.

Formula 2



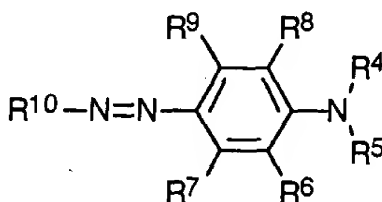
Each of  $R^1$ ,  $R^2$ ,  $R^3$ ,  $X$ ,  $Y$  and  $Z$  has the same meanings as is defined in the Formula 1. Each of  $R^4$  and  $R^5$  independently is a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, or an aryl group; otherwise a set of  $R^4$  and  $R^5$ , a set of  $R^3$  and  $R^4$  or a set of  $R^3$  and  $R^5$  are combined to form a ring.

Formula 3



In the formula, each of R<sup>6</sup>, R<sup>7</sup>, R<sup>8</sup> and R<sup>9</sup> independently is a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, a heterocyclic group, cyano, hydroxyl, nitro, amino, an alkylamino, an alkoxy group, an aryloxy group, amido, an arylamino group, ureido, sulfamoylamino, an alkylthio group, an alkoxycarbonyl group, a heterocyclic ring-oxy group, an azo group, an acyloxy group, a carbamoyloxy group, a silyloxy group, an aryloxycarbonyl group, an aryloxycarbonylamino group, an imido group, a heterocyclic ring-thio group, sulfinyl, phosphoryl, an acyl group, carboxyl or sulfo. Otherwise R<sup>8</sup> and R<sup>9</sup> are combined to form an aromatic ring or a heterocyclic ring. R<sup>10</sup> is an unsaturated heterocyclic ring. M is a hydrogen atom, a dissociated inorganic base, a primary amine, a secondary amine, or a tertiary amine.

Formula 4



In the formula, each of R<sup>4</sup> to R<sup>10</sup> has the same meanings as is defined in the Formulas 2 and 3.

20

[Claim 4] The jet printing ink of claim 1 or 2, wherein the polymer having the tertiary amino group, the nitrogen atom-containing heterocyclic group or the quater-

nary cationic group thereof has a molecular weight in the range of 1,000 to 100,000.

[Claim 5] The jet printing ink of claim 1 or 2,  
5 wherein the polymer having the tertiary amino group, the nitrogen atom-containing heterocyclic group or the quaternary cationic group thereof is contained in an amount of 0.1 to 50 weight %.

10 [Claim 6] The jet printing ink of claim 1 or 2, which has a viscosity of 50 cp or lower at 25°C.

[Claim 7] A method of forming an ink image on a receiving sheet using the jet printing ink of claim 1 or 2  
15

[Detailed description of invention]

[Field of invention]

The present invention relates to a jet printing ink and an ink image-forming method using thereof.

20

[Prior art]

An ink-jet recording method has been developed and widely used because it has various merits. For example, materials for the method are available at a low cost, and  
25 high speed recording can be accomplished. Further, the method makes relatively low noise, and easily utilizable for full-color recording.

As the ink-jet recording method, three types are known. One is a method in which drops of ink are ejected under  
30 pressure by means of a piezoelectric element. In another method, bubbles are formed in ink by heating so that the bubbles would push out drops of the ink. The other is a method in which drops of ink are sucked and ejected with electrostatic force. As the ink for the method (i.e., jet

printing ink), various kinds of ink such as aqueous ink, oily ink, and solid (melting) ink have been used.

Dyes used for the ink should satisfy various conditions. For example, they should be highly soluble in a solvent, and they should have excellent hues. It is also necessary for the dyes to have high resistance against light, heat, air, water and chemicals. Further, they should be well fixed onto an image-receiving sheet without blotting. They are furthermore required to have long shelf lives, to have no toxicity, to have high purity, and to be available at a low cost. The above-mentioned requirements ought to be considered in ink-jet printing systems using different receiving sheets.

15 [Object to be attained by invention]

It is an object of the present invention to provide an improved jet printing ink, which forms a clear image not depending on a nature of a receiving sheet. It is another object of the invention to provide an improved jet printing ink, which forms a clear image with good hue. It is further object of the invention to provide an improved jet printing in, which forms a clear image with fixation to a variety of paper sheets. It is a furthermore object of the invention to provide an ink-jet recording method, which can  
25 attain the above-mentioned objects.

[Means to attain object]

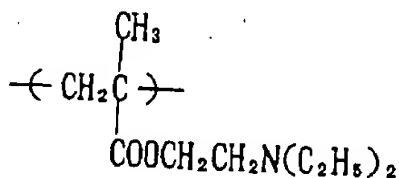
The objects are attained by a jet printing ink comprising a water-soluble dye and an aqueous medium, which  
30 further comprises a polymer having a tertiary amino group, a nitrogen atom-containing heterocyclic group or a quaternary cationic group thereof.

[Embodiment of invention]

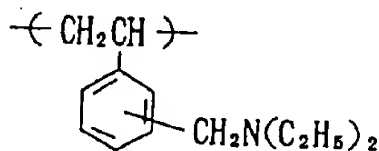
The characteristic feature of the invention resides in the use of a polymer having a tertiary amino group, a nitrogen atom-containing heterocyclic group or a quaternary cationic group thereof.

Preferred examples of homopolymers and copolymers comprising a vinyl monomer unit having a tertiary amino group are shown below. The number of the monomer unit means a mole % (the same as the other units shown below).

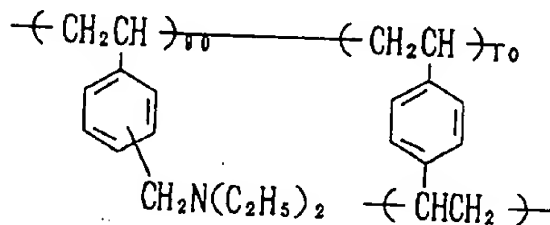
a - 1



a - 2



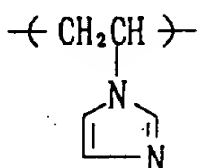
a - 3



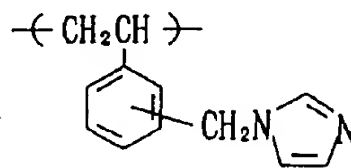


Examples of homopolymers and copolymers comprising a vinyl monomer unit having a tertiary imidazolyl group are described in Unites States Patents No. 4,282,305, No. 4,115,124, and No. 3,148,061, and Japanese Patent Provisional Publications No. 60-118834 and No. 60-122941, and are shown below.

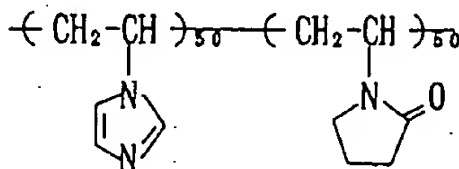
(A-4)



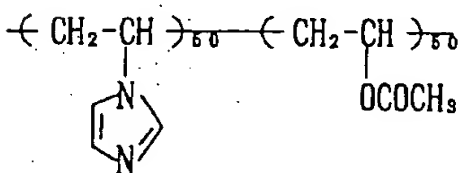
(A-5)



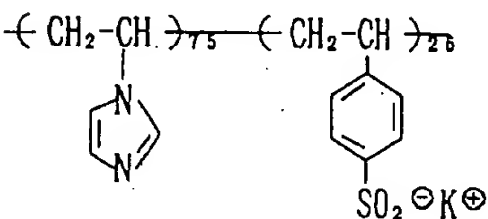
(A-6)

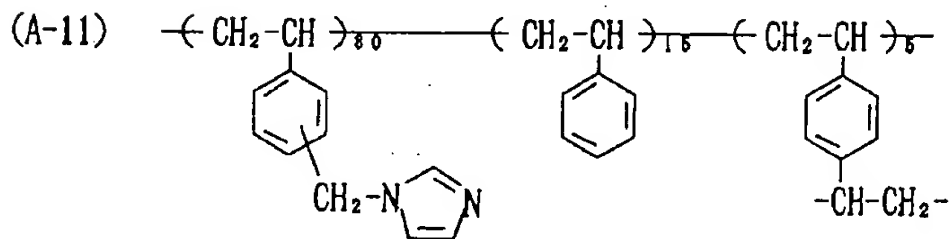
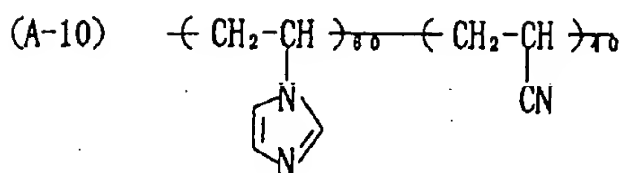
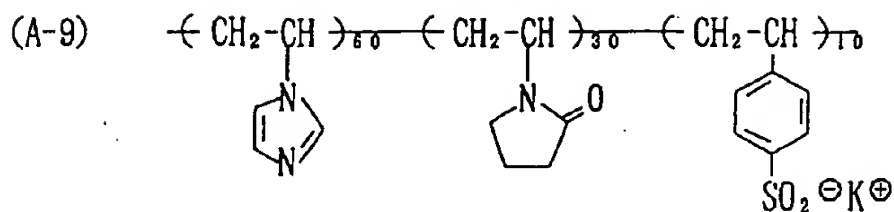


(A-7)

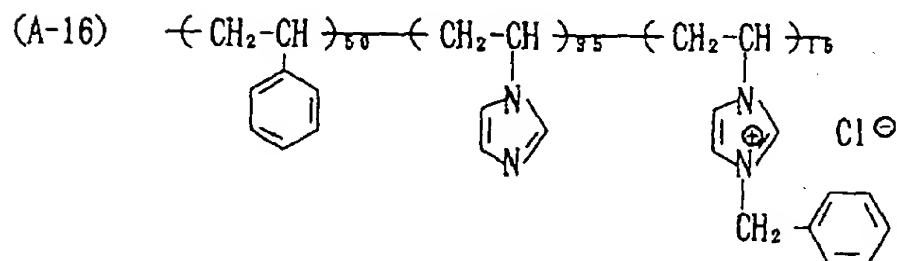
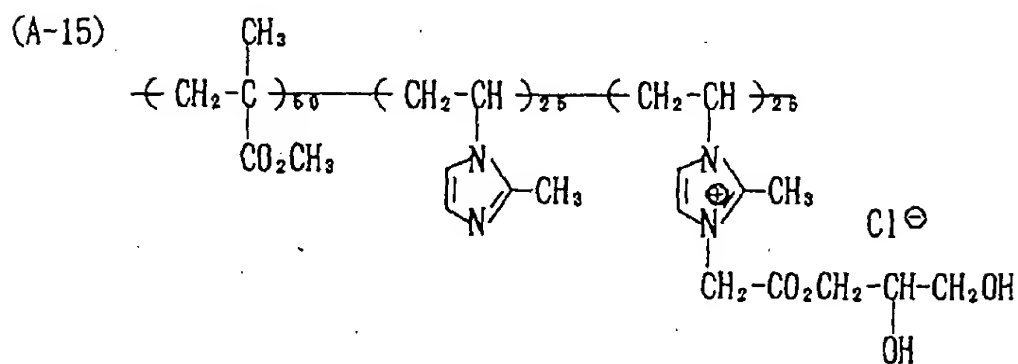
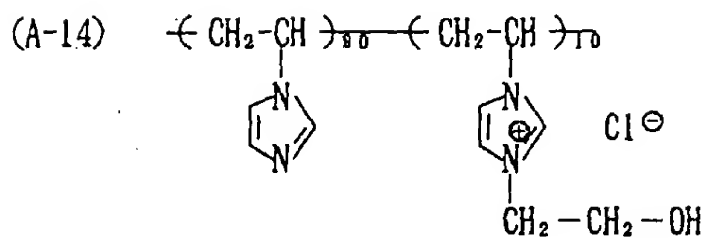
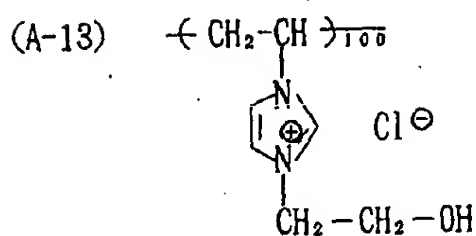
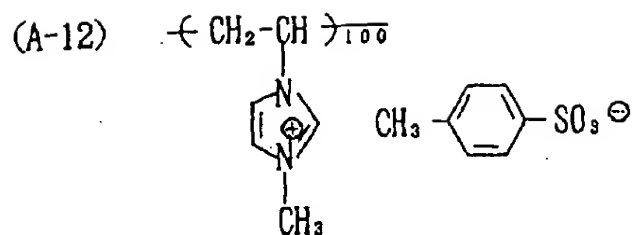


(A-8)



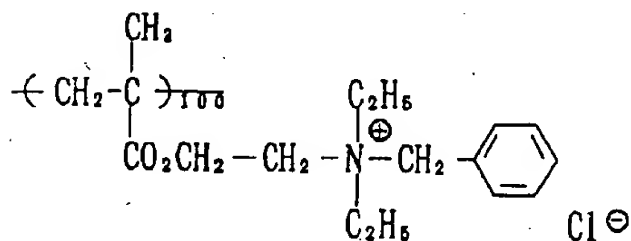


Examples of homopolymers and copolymers comprising a vinyl monomer unit having a quaternary imidazolium group are described in British Patents No. 2,056,101, No. 2,093,041, and No. 1,594,961, United States Patents No. 4,124,386, No. 4,115,124, No. 4,273,853, and No. 4,450,224, and Japanese Patent Provisional Publication No. 48-28325, and are shown below.

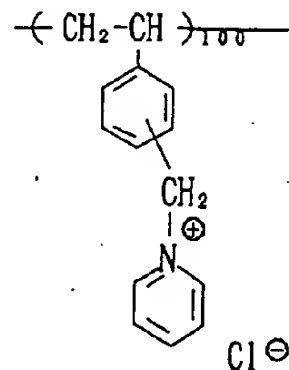


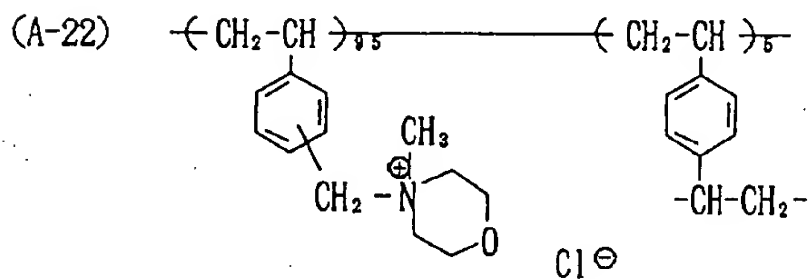
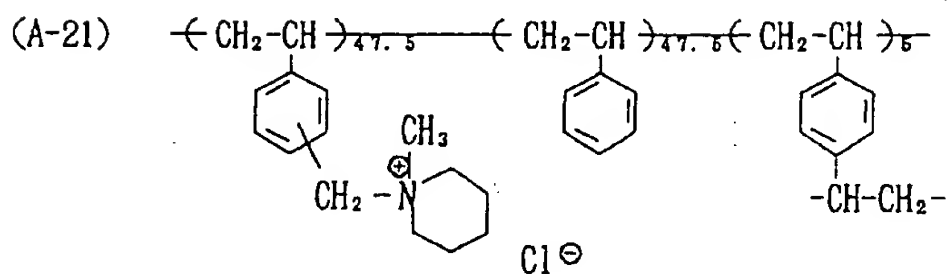
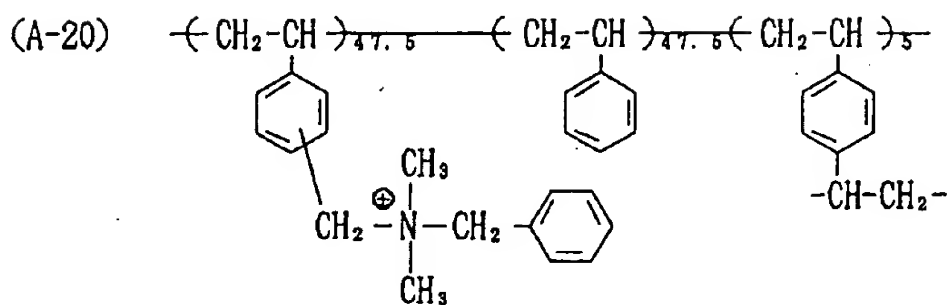
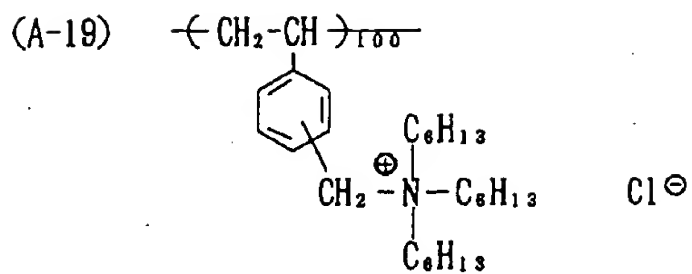
Examples of homopolymers and copolymers comprising a vinyl monomer unit having a quaternary ammonium salt are described in United States Patents No. 3,709,690, No. 3,898,088, and No. 3,958,995, and Japanese Patent Provisional Publications No. 60-57836, No. 60-60643, No. 60-122940, No. 60-122942, and No. 60-235134, and are shown below.

(A-17)



(A-18)





The polymers further include a polymer having a pyridine ring or a pyridinium group described in United States Patents No. 2,548,564, No. 2,484,403, No. 3,148,161, and No. 3,756,814; a polymer which can form a cross-link with gelatin described in United States Patents No. 3,625,694, No. 3,859,096, and No. 4,128,538, and British Patent No. 1,277,453; an aqueous sol-type compound described in United States Patents No. 2,721,852, No. 2,798,063, and No. 3,958,995, and Japanese Patent Provisional Publications No. 54-26027, No. 54-115228, and No. 54-145529; a reactive polymer having a covalent bond with a dye described in United States Patent No. 4,168,976 and Japanese Patent Provisional Publication 54-137333; and another polymer described in United States Patents No. 3,271,147, No. 3,271,148, No. 3,488,706, No. 3,557,066, No. 3,642,482, No. 3,709,690, and No. 3,788,855, and Japanese Patent Provisional Publications No. 50-71332, No. 53-30328, No. 52-155528, No. 53-125, and No. 53-1024. The polymers further include a compound described in United States Patent No. 2,675,316 and No. 2,882,156.

The polymer having the tertiary amino group, the nitrogen atom-containing heterocyclic group or the quaternary cationic group thereof preferably has a mean molecular weight in the range of 1,000 to 100,000, more preferably 5,000 to 50,000.

The polymer having the tertiary amino group, the nitrogen atom-containing heterocyclic group or the quaternary cationic group thereof is preferably contained in the jet-printing ink in an amount of 0.1 to 50 weight %, more preferably 0.1 to 20 weight %.

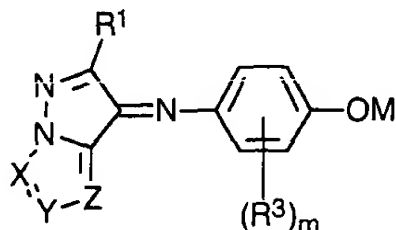
The jet-printing ink of the invention containing the polymer preferably has a viscosity of 50 cp or less (measured at 25°C), more preferably 20 cp or less. The polymer is preferably used in the range of 0.1 to 100 moles (in terms of the basic functional group such as the tertiary

amino group, quaternary ammonium group, or the nitrogen atom-containing heterocyclic group), more preferably 1 to 50 moles, based on one mole of the dye.

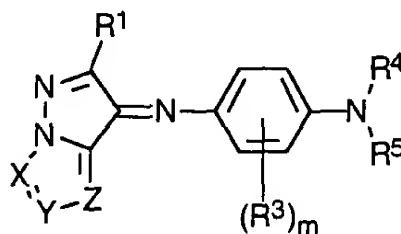
Two or more polymers can be used in combination.

5 The water-soluble dye in the present invention is preferably represented by a formula 1 to 4.

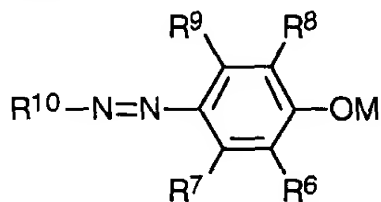
Formula 1



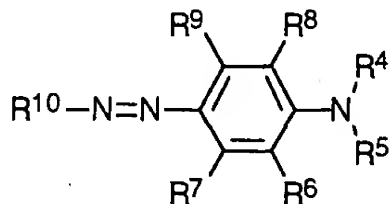
Formula 2



Formula 3



Formula 4



In the formulas, each of R<sup>1</sup> and R<sup>3</sup> independently is a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, cyano, amido,

sulfonamido, ureido, an alkoxycarbonylamino group, an alkylthio group, an arylthio group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an acyl group, an amino group, or an alkylamino group. (A  
5 benzene ring contained in the substituent group can further have a substituent group selected from the group consisting of a halogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, cyano, amido, sulfonamido,  
10 ureido, an alkoxycarbonylamino group, an alkylthio group, an arylthio group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an acyl group, an amino group and an alkylamino group).  $m$  is an integer of 0 to 4. In the case  $m$  is 2 to 4, the groups of  $R^3$  can  
15 be different from each other.

Each of  $X$ ,  $Y$  and  $Z$  independently is  $=N-$  or  $=CR^2-$ , in which  $R^2$  is a hydrogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, a heterocyclic group, an alkoxy group, or an aryloxy group; in the case  
20 that both of  $X$  and  $Y$  are  $=CR^2-$ , these two  $R^2$  can be combined to form a ring; and  $M$  is a hydrogen atom, a dissociated inorganic base, a primary amine, a secondary amine, or a tertiary amine.

Each of  $R^4$  and  $R^5$  independently is a hydrogen atom, an  
25 alkyl group, a cycloalkyl group, an aralkyl group, or an aryl group; otherwise a set of  $R^4$  and  $R^5$ , a set of  $R^3$  and  $R^4$  or a set of  $R^3$  and  $R^5$  are combined to form a ring. (In the formulas 2 and 4, at least one of  $R^1$  to  $R^{10}$  preferably has a group having a function of dissolving the compound in  
30 water.

In the formula, each of  $R^6$ ,  $R^7$ ,  $R^8$  and  $R^9$  independently is a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, a heterocyclic group, cyano, hydroxyl, nitro, amino, an alkyl-  
35 lamino, an alkoxy group, an aryloxy group, amido, an ary-



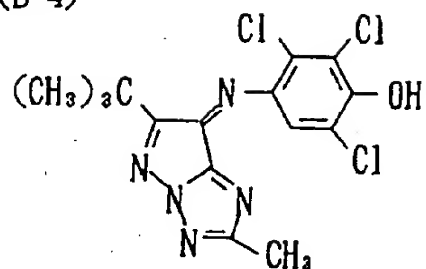
lamino group, ureido, sulfamoylamino, an alkylthio group, an alkoxycarbonyl group, a heterocyclic ring-oxy group, an azo group, an acyloxy group, a carbamoyloxy group, a silyloxy group, an aryloxycarbonyl group, an aryloxycarbony-  
5 lamino group, an imido group, a heterocyclic ring-thio group, sulfinyl, phosphoryl, an acyl group, carboxyl or sulfo. Otherwise  $R^8$  and  $R^9$  are combined to form an aromatic ring or a heterocyclic ring.  $R^{10}$  is an unsaturated heterocyclic ring.

10 In the formula,  $R^1$  can have a substituent group selected from a group consisting of a hydrogen atom, a halogen atom, an alkyl group, a cycloalkyl group, an aralkyl group, an aryl group, a heterocyclic group, an alkoxy group, an aryloxy group, cyano, amido, sulfonamido, ureido, an  
15 alkoxycarbonylamino group, an alkylthio group, an arylthio group, an alkoxycarbonyl group, a carbamoyl group, a sulfamoyl group, a sulfonyl group, an acyl group, an amino group and an alkylamino group; each of X, Y and Z independently is =N- or =CR<sup>2</sup>-, in which  $R^2$  is a hydrogen atom, an alkyl  
20 group, a cycloalkyl group, an aralkyl group, an aryl group, a heterocyclic group, an alkoxy group, or an aryloxy group; in the case that both of X and Y are =CR<sup>2</sup>-, these two  $R^2$  can be combined to form a ring; and M is a hydrogen atom, a dissociated inorganic base, a primary amine, a secondary  
25 amine, or a tertiary amine.

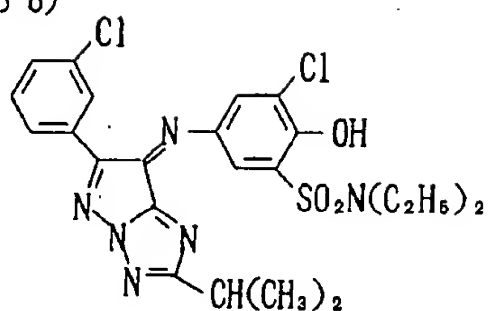
The compounds are described in detail in Japanese Patent Applications Nos. H10-178188, H9-363419 and H9-324877.

Examples of the dyes of the formulas 1 to 4 used in the present invention are shown below without limiting the  
30 present invention.

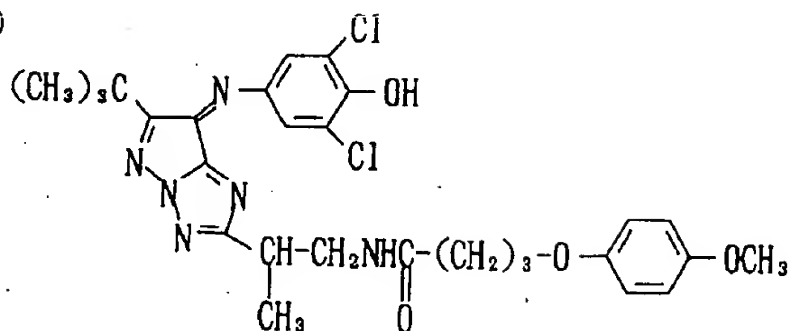
(B-4)



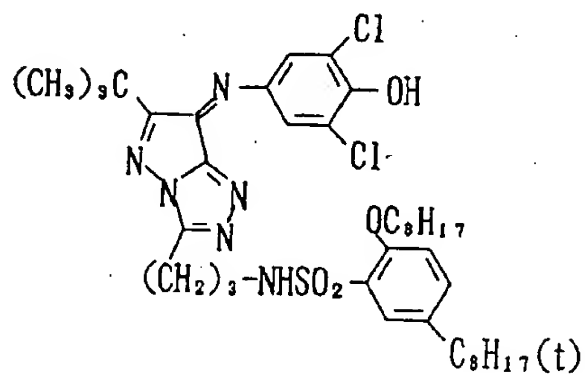
(B-8)



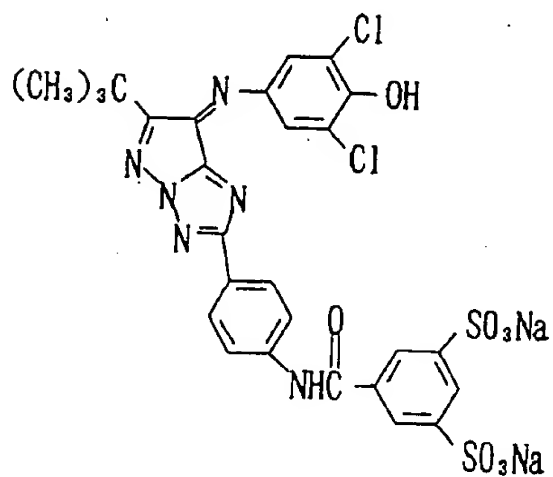
(B-9)



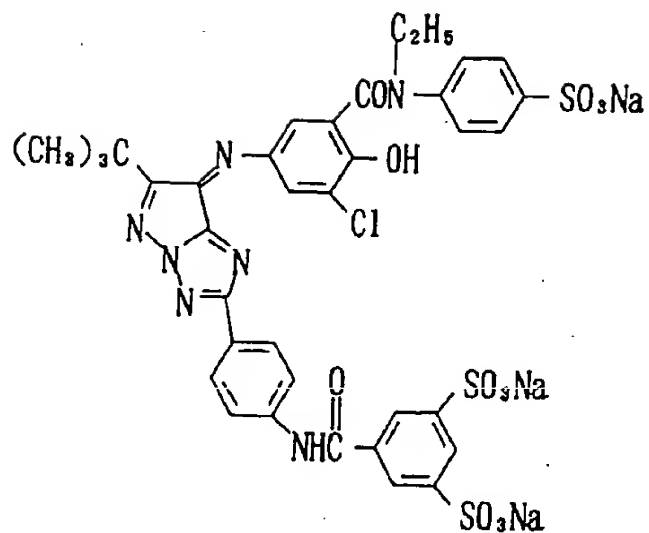
(B-18)



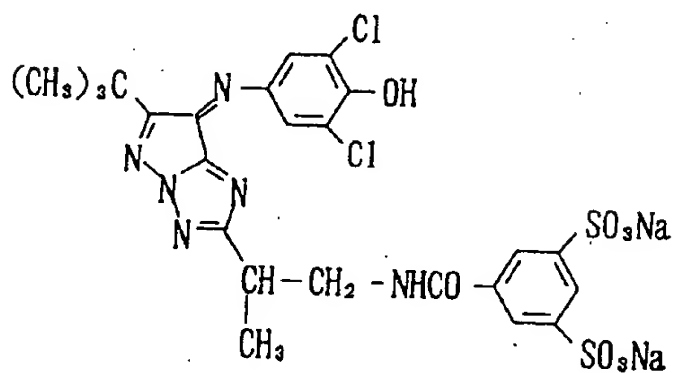
(B-28)



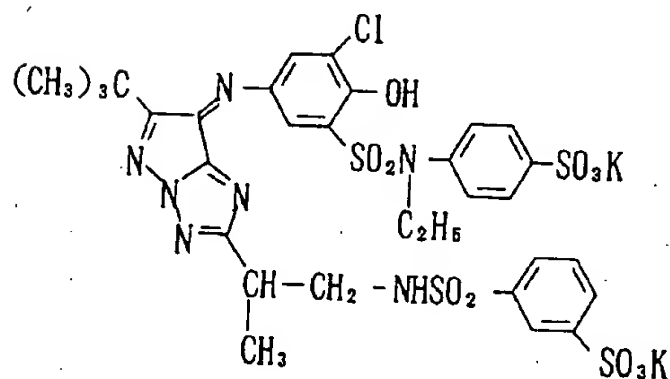
(B-30)



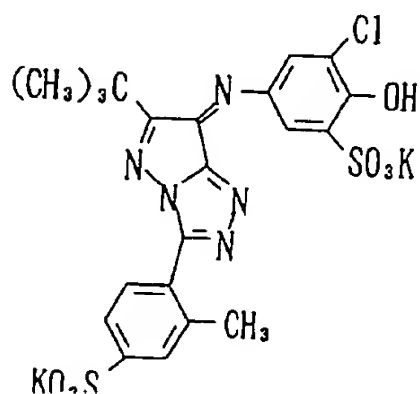
(B-31)



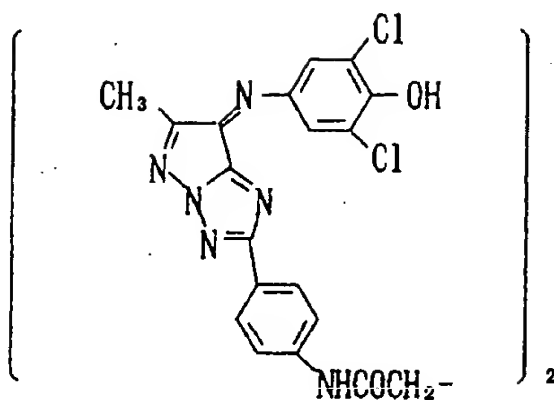
(B-34)



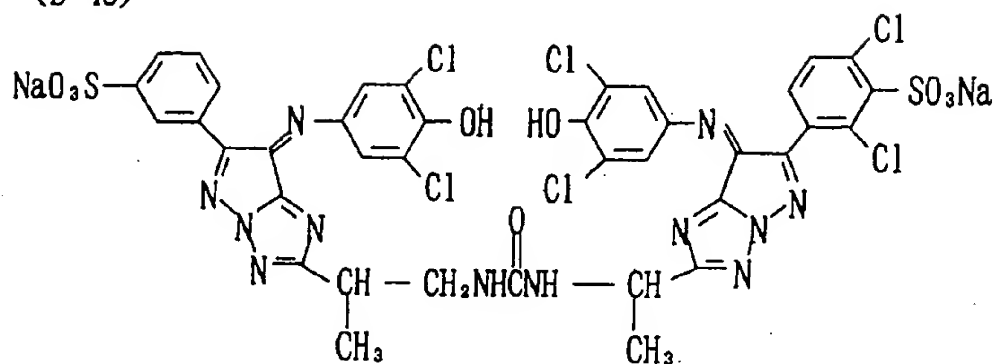
(B-38)



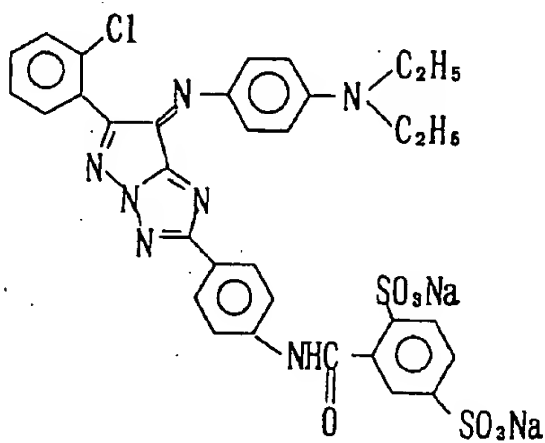
(B-42)



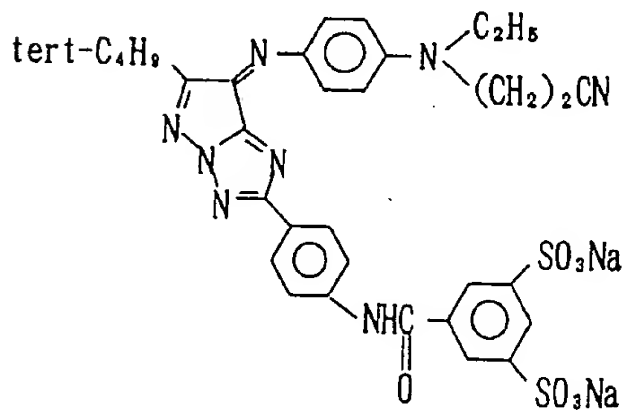
(B-43)

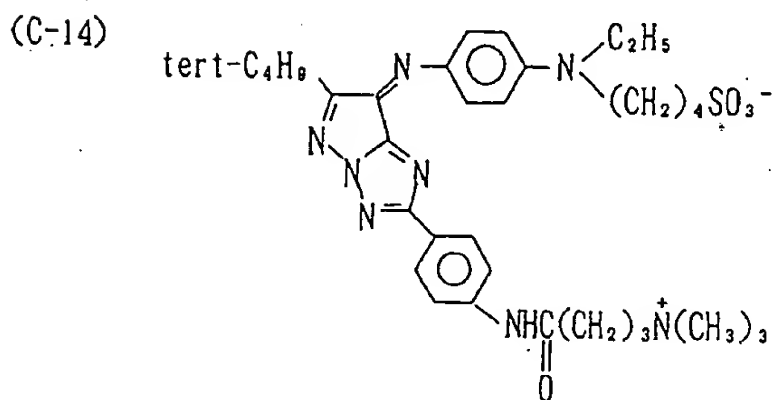
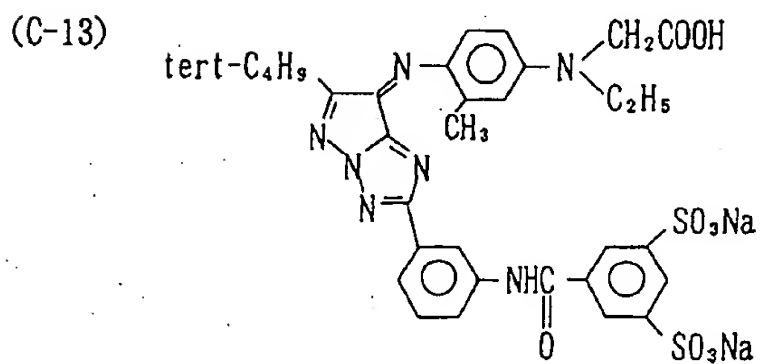
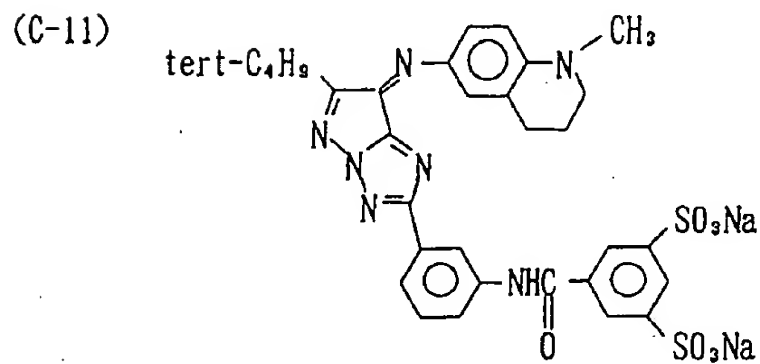
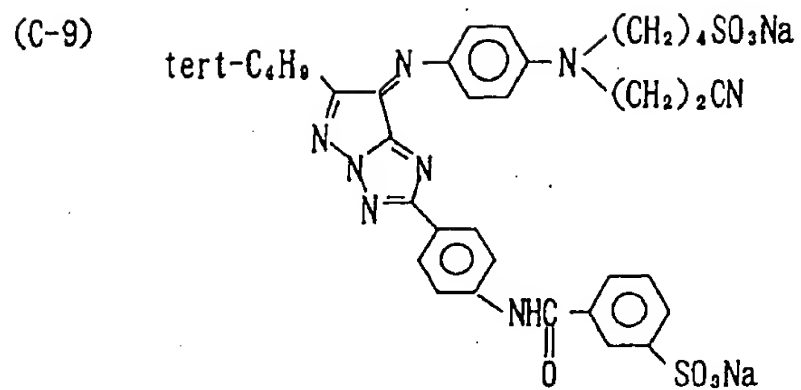


(C-3)

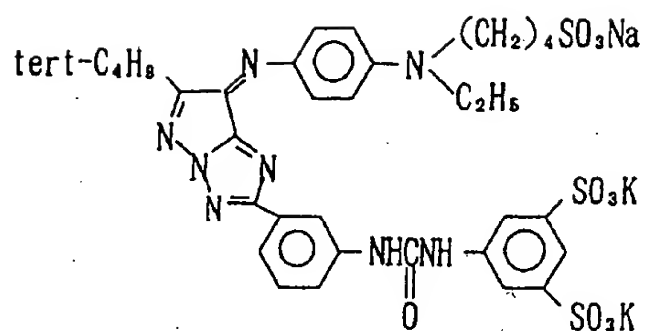


(C-8)

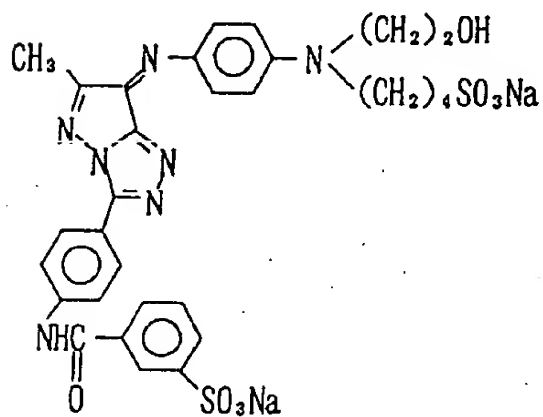




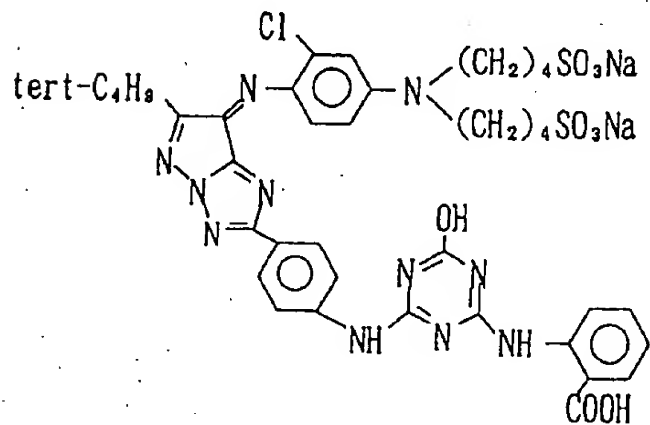
(C-21)



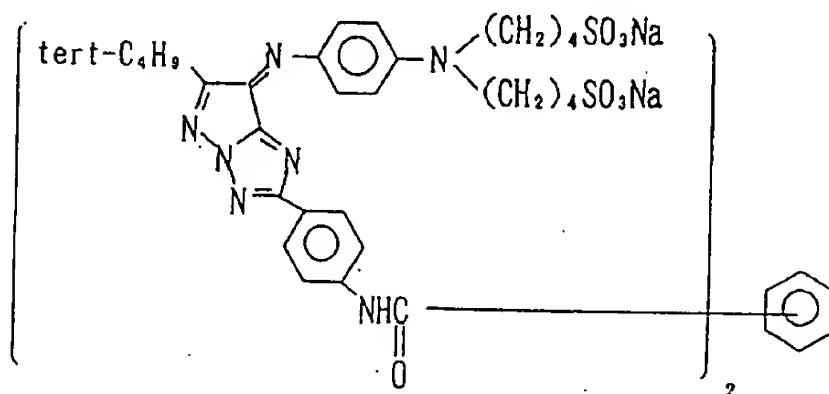
(C-25)



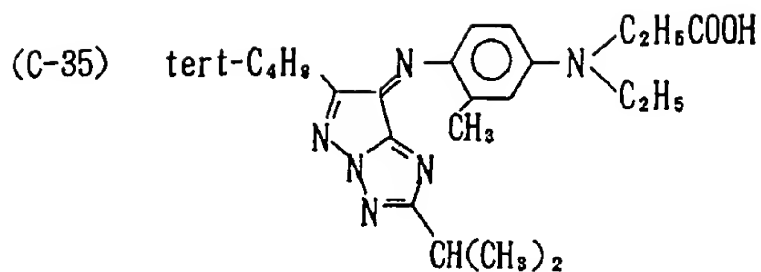
(C-31)



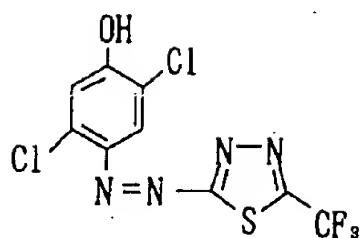
(C-32)



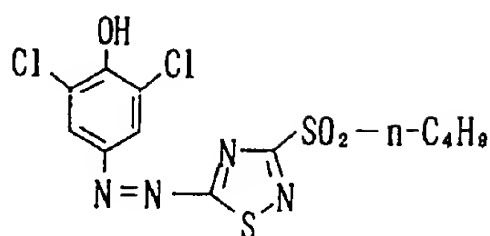
(p-substituted form)



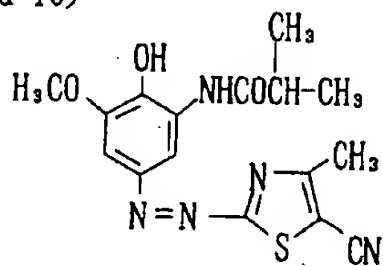
(d-2)



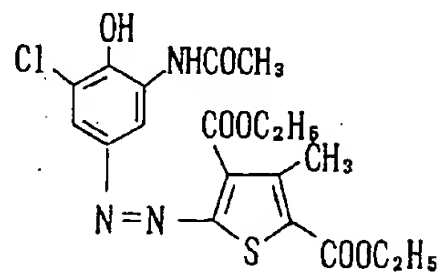
(d-5)



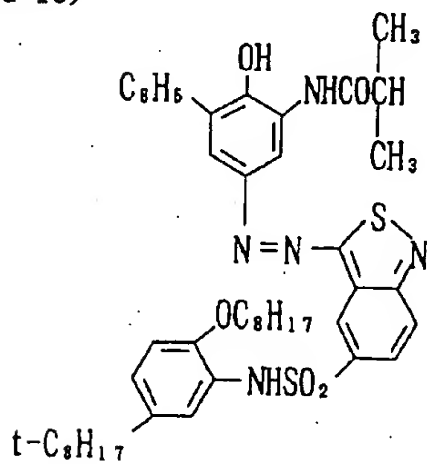
(d-10)



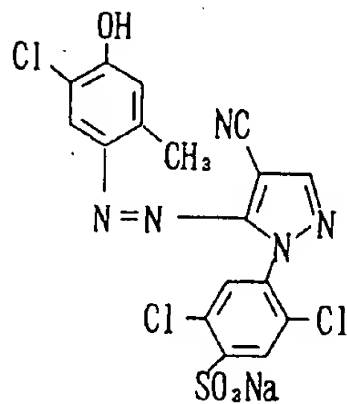
(d-13)



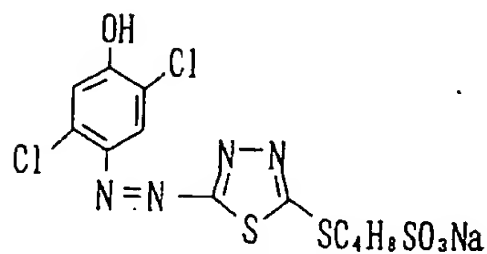
(d-18)



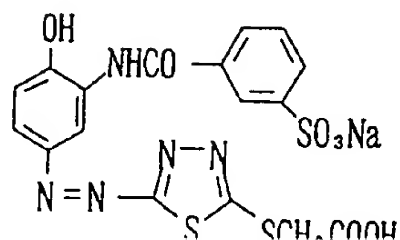
(d-21)



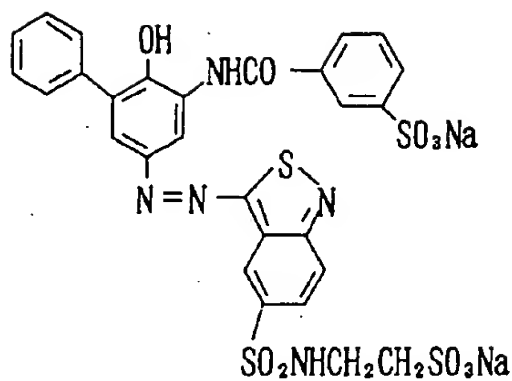
(d-26)



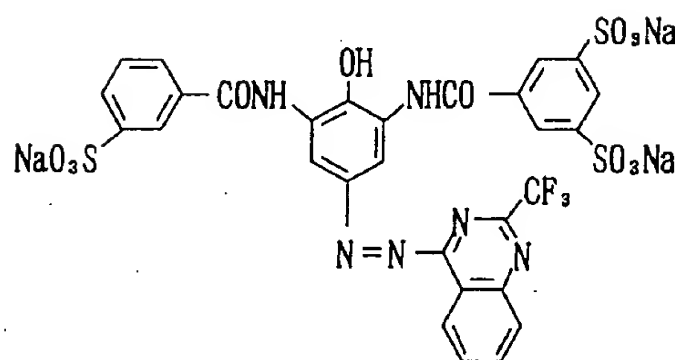
(d-35)



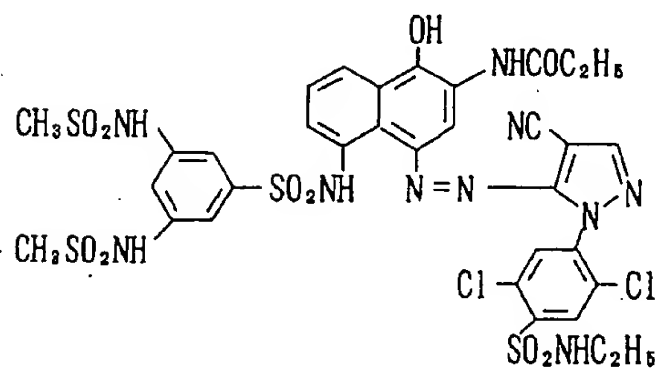
(d-37)



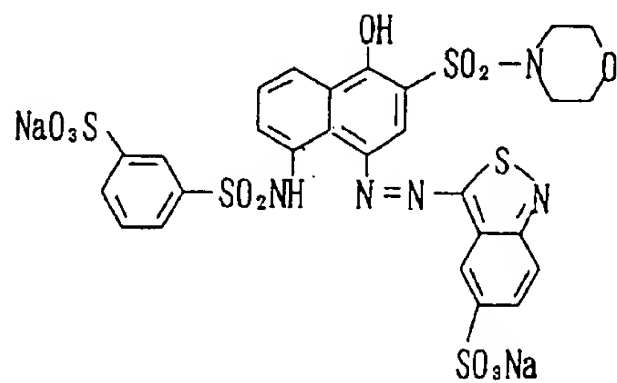
(d-42)



(d-53)

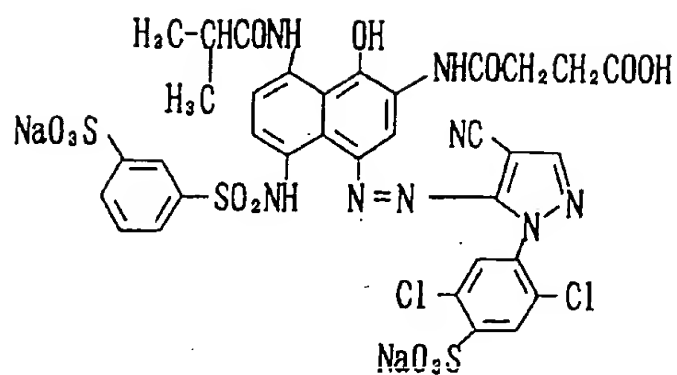


(d-55)

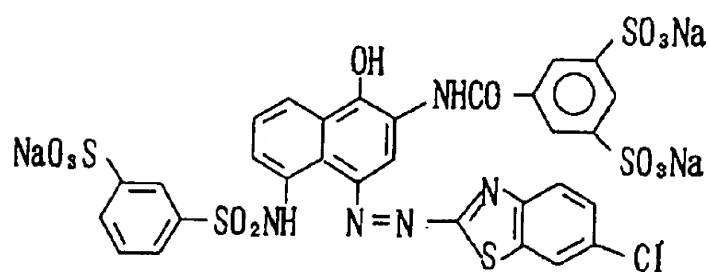




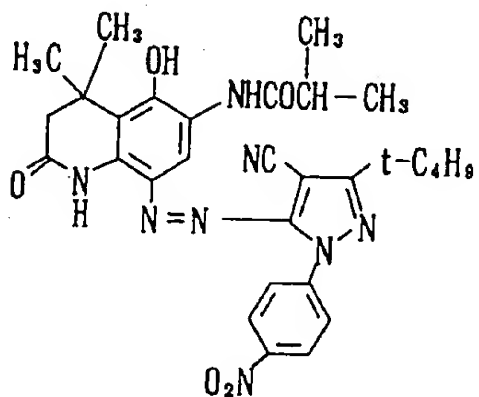
(d-64)



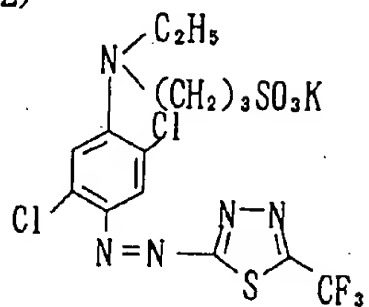
(d-69)



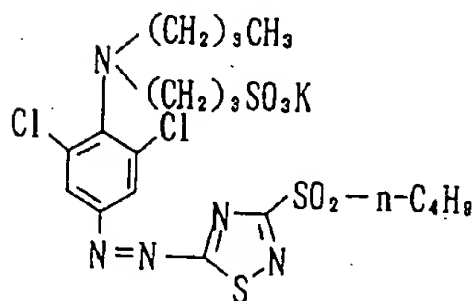
(d-71)



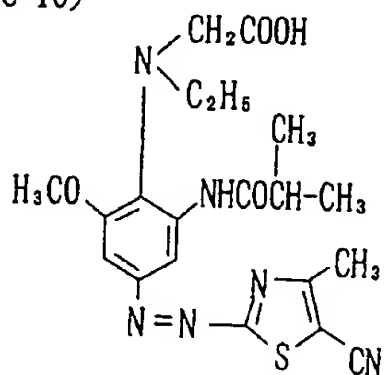
(e-2)



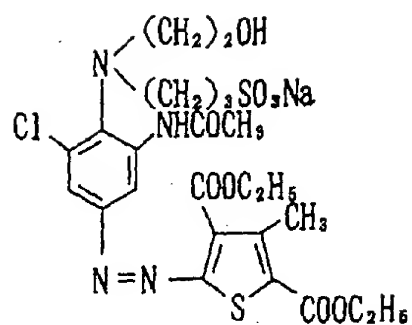
(e-5)



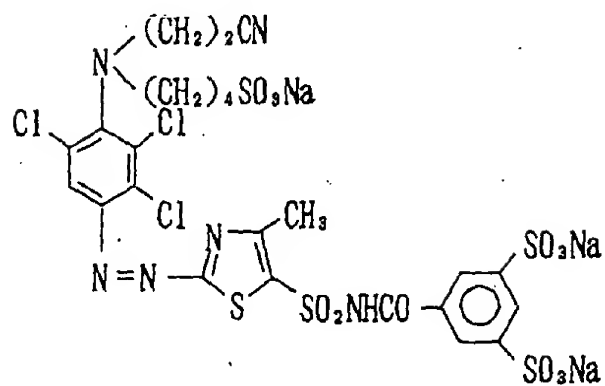
(e-10)



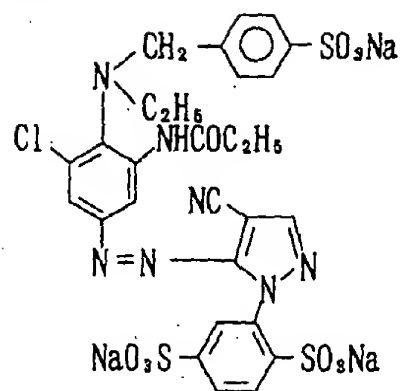
(e-13)



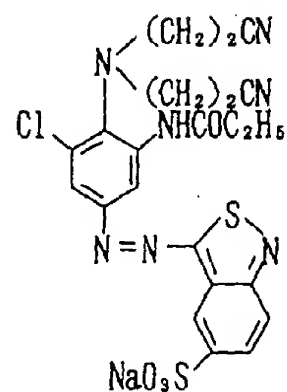
(e-22)



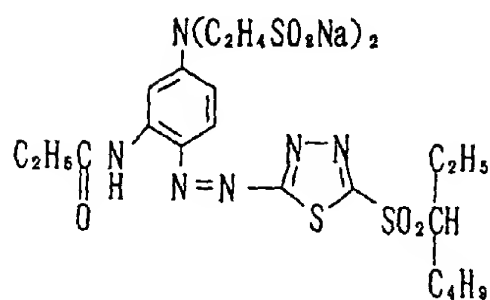
(e-24)



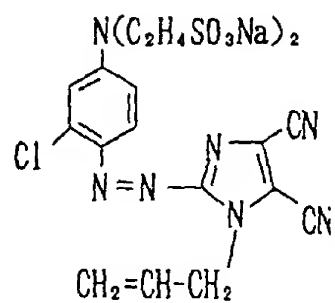
(e-25)



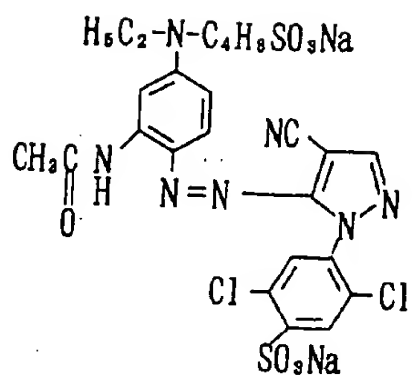
(e-37)



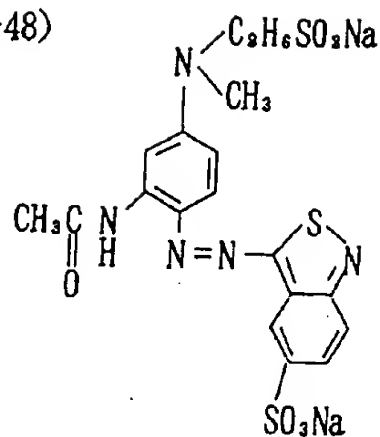
(e-42)



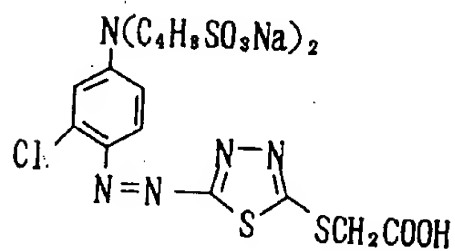
(e-47)



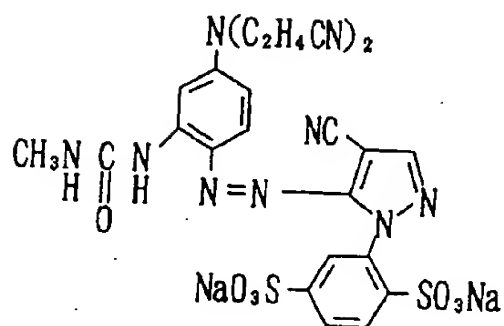
(e-48)



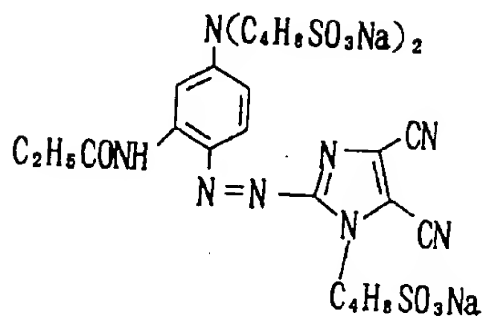
(e-51)



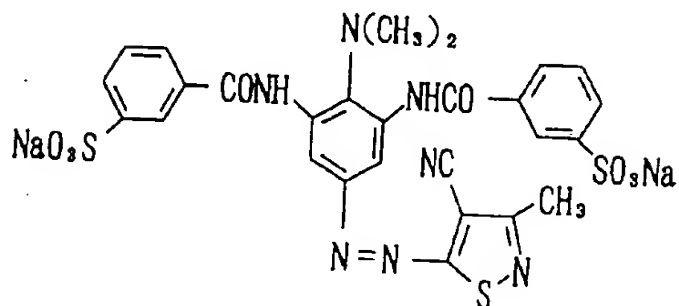
(e-56)



(e-60)



(e-66)



Two or more dyes can be employed in combination. In the ink, the dye is preferably contained in an amount of 0.1 to 30 weight %.

The dye shows a hue of magenta or cyan. Therefore, a  
5 combination of the azomethine dye or azo dye with a dye giving a yellow hue such as that described in Japanese Patent Provisional Publication No. H10-95942 is preferably employed for preparing a color image.

The medium of aqueous ink is an aqueous medium, such  
10 as water or a mixture of water and an organic solvent compatible with water. Examples of the water-compatible organic solvents include alcohols (e.g., methanol, ethanol, propanol, isopropanol, butanol, iso-butanol, sec-butanol, t-butanol, pentanol, hexanol, cyclohexanol, benzyl alcohol),  
15 polyhydric alcohols (e.g., ethylene glycol, diethylene glycol, triethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, butylene glycol, hexanediol, pentane diol, glycerol, hexanetriol, thiodiglycol), glycol derivatives (e.g., ethylene glycol  
20 monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monomethyl ether, diethylene glycol monobutyl ether, propylene glycol monomethyl ether, propylene glycol monobutyl ether, dipropylene glycol monomethyl ether, triethylene glycol monomethyl  
25 ether, ethylene glycol diacetate, ethylene glycol monomethyl ether acetate, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, ethylene glycol monophenyl ether), amines (e.g., ethanolamine, diethanolamine, triethanolamine, N-methyldiethanolamine, N-  
30 ethyldiethanolamine, morpholine, N-ethylmorpholine, ethylenediamine, diethylenetriamine, triethylenetetramine, polyethyleneimine, tetramethylpropylenediamine), and other polar solvents (e.g., formamide, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, sulfolane, 2-  
35 pyrrolidone, N-methyl-2-pyrrolidone, N-vinyl-2-pyrrolidone,

2-oxazolidone, and 1,3-dimethyl-2-imidazolidinone, acetonitrile, acetone).

Two or more kinds of water-compatible organic solvents may be used in combination with water.

5       The dye may be dissolved or dispersed in an aqueous solvent (i.e., water or a mixture of water and a water-compatible organic solvent) to prepare aqueous ink. For dispersing, the dye is preferably made to be in the form of fine particles by means of a dispersing machine (e.g., ball  
10 mill, sand mill, attriter, roll mill, agitator mill, Henschek mixer, colloid mill, ultrasonic homogenizer, pearl mill, jet mill, ong mill). The dye may be dissolved in an organic solvent, and then the solution may be emulsified in an aqueous solution. For emulsifying, dispersing agents  
15 (emulsifiers) or surface active agents can be used. The preparation method of aqueous jet printing ink is described in Japanese Patent Provisional Publications No. H5-148436, No. H5-295312, No. H7-97541, No. H7-82515, and No. H7-118584.

20       A known organic solvent can be used as a medium of an oily ink. Examples of the organic solvents include alcohols (e.g., ethanol, pentanol, heptanol, cyclohexanol, benzyl alcohol, phenethyl alcohol, phenylpropyl alcohol, furfuryl alcohol, and anise alcohol), glycohols (e.g., ethylene glycol monoethyl ether, ethylene glycol monophenyl  
25 ether, diethylene glycol monoethyl ether, diethylene glycol monobutyl ether, propylene glycol monoethyl ether, propylene glycol monophenyl ether, dipropylene glycol monomethyl ether, dipropylene glycol monoethyl ether, triethylene glycol monoethyl ether, ethylene glycol diacetate, ethylene glycol monoethyl ether acetate, and propylene glycol diacetate), ketones (e.g., benzyl methyl ketone, diacetone alcohol, and cyclohexanone), ethers (e.g., butyl phenyl ether, benzyl ethyl ether, and dihexyl ether), esters (e.g., ethyl  
30 acetate, amyl acetate, benzyl acetate, phenylethyl acetate,

phenoxyethyl acetate, ethyl phenylacetate, benzyl propionate, ethyl benzoate, butyl benzoate, ethyl laureate, butyl laureate, isopropyl myristate, isopropyl palmitate, triethyl phosphate, tributyl phosphate, diethyl phthalate, dibutyl phthalate, diethyl malonate, dipropyl malonate, diethyl-malonate diethyl succinate, dibutyl succinate, diethyl glutarate, diethyl adipate, dibutyl adipate, di-2-methoxyethyl adipate, diethyl sebacate, diethyl maleate, dibutyl maleate, dioctyl maleate, diethyl fumarate, dioctyl fumarate, and 3-hexenyl cinnamate), hydrocarbon solvents (e.g., petroleum ether, petroleum benzin, tetralin, decalin, 1-amylnbenzene, and dimethylnaphthalene), and other polar solvents (e.g., acetonitrile, formamide, N,N-dimethylformamide, N,N-dimethylacetamide, dimethylsulfoxide, sulfolane, propylene carbonate, N-methyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, and N,N-diethyldodecanamide.

Two or more organic solvents can be employed in combination.

An oily ink can be prepared by dissolving the dye in the organic solvent. The oily ink can also be prepared by dispersing the dye in the organic solvent. An appropriate dispersing agent can be used to disperse the dye in the solvent. The process for the preparation of an oily jet printing ink is described in Japanese Patent Provisional Publication Nos. H3-231975 and H5-508883.

A medium of a solid ink is a phase change medium, which is solid at the room temperature, and is melt to change into liquid when the ink is heated and jetted. Examples of the phase change mediums include natural waxes (e.g., bee wax, carnauba wax, rice wax, wood wax, jojoba oil, spermaceti, candelilla wax, lanolin, montan wax, ozocerite, ceresine, paraffin wax, microcrystalline wax, petrolatum), synthetic waxes (e.g., polyethylene wax), chlorinated hydrocarbons, organic acids (e.g., palmitic acid, stearic acid, behenic acid, tiglic acid, 2-

30 and sulfonamide (e.g., p-toluene sulfonamide, ethylbenzenene sulfoamide, butylbenzene sulfonamide).

The phase change temperature (usually melting point) of the phase change medium is preferably in the range of 60 to 200°C, and more preferably in the range of 80 to 150°C.

The solid ink can be prepared by dissolving the dye in a phase change medium, which is previously melt by heating. An appropriate binder can be used to dissolve the ink. The solid ink can also be prepare by dispersing the dye in the  
5 phase change medium, which is previously melt. An appropriate dispersing agent or binder can be used to disperse the ink. The process for the preparation of the solid ink is described in Japanese Patent Provisional Publication Nos. H5-186723 and H7-70490.

10 The jet printing ink can use another dye in addition to the above-mentioned dye.

In the jet printing ink, various additives can be contained, if desired. Examples of the additives include viscosity controlling agent, surface tension controlling agent,  
15 specific resistance controlling agent, film-formation controlling agent, UV absorber, anti-oxidizing agent, anti-fading agent, antifungal agent, rust inhibitor, dispersing agent, and surface active agent. Additives for the jet printing ink are described in Japanese Patent Provisional  
20 Publication No. H10-95942.

The anti-fading agent and UV absorber are described in Japanese Patent Provisional Publications No. H1-13546, No. H1-159655, and No. H1-171887.

The viscosity of the aqueous or oily ink is preferably  
25 adjusted to 50 cp or less. The aqueous or oily ink preferably has a surface tension in the range of 20 to 100 dyn/cm.

The dye of the formulas 1 to 4 and a dye of another hue used in combination with the dyes show an excellent hue where the dyes are dissociated as an anion or in a state  
30 with a mordant. Accordingly, a dissociating agent for the dye (e.g., an inorganic base, a primary amine, a secondary amine or a tertiary amine) is preferably added to the jet printing ink, or the dissociating agent for the dye or a mordant for the dye is preferably added to an image-



receiving sheet. Examples of the mordant include inorganic pigments (e.g., silica pigment, alumina pigment).

The mordant to be contained in the image-receiving sheet preferably is non-diffusing. Accordingly, a polymer  
5 mordant is preferably added to the image-receiving sheet.

For forming a full-color image, inks of magenta, cyan and yellow hues can be used. Further, ink of black hue can be used to control the hues of the image.

As recording paper (image-receiving sheet) for ink-jet  
10 printing, coat paper is preferred from the viewpoints of image quality and storing durability of image. The receiving sheet preferably contains a polymer mordant. The polymer mordant is described in Japanese Patent Provisional Publication Nos. 48-28325, 54-74430, 54-124726, 55-22766,  
15 55-142339, 60-23850, 60-23851, 60-23852, 60-23853, 60-57836, 60-60643, 60-118834, 60-122940, 60-122941, 60-122942, 60-235134, H1-161236, United States Patent Nos. 2,484,430, 2,548,564, 3,148,061, 3,309,690, 4,115,124, 4,124,386, 4,193,800, 4,273,853, 4,282,305 and 4,450,224. The image  
20 receiving sheet containing a polymer mordant described in Japanese Patent Provisional Publication No. H1-161236, pp. 212-215 is preferred. An image of excellent quality can be formed, and light-resistance of the image can be improved by using the polymer mordant disclosed in the publication.

25 The image-receiving sheet for ink-jet recording may contain an inorganic pigment. Examples of the inorganic pigment include silica pigment, alumina pigment, titanium dioxide pigment, zinc oxide pigment, zirconium oxide pigment, mica-shaped iron oxide, white lead, lead oxide pig-  
30 ment, cobalt oxide pigment, strontium chromate, molybdenum pigments, smectites, magnesium oxide pigment, calcium oxide pigment, calcium carbonate pigment, and mullite. Two or more pigments may be used in combination.

The image-receiving sheet preferably comprises a hy-  
35 drophilic layer (an ink-receiving layer) containing a hy-

drophilic binder. The binder preferably is a water absorp-  
tive polymer. Examples of the hydrophilic binders include  
gelatin, gelatin derivatives, polyvinyl alcohol, polyvinyl  
alcohol derivatives, polyalkyleneoxide, and polyalkyleneox-  
5 ide derivatives. The hydrophilic binder is described in  
Japanese Patent Provisional Publication No. H1-161236, pp.  
215-222.

The image-receiving material preferably contains a  
matting agent. The matting agent is described in Japanese  
10 Patent Provisional Publication No. H1-161236, pp. 263-264.

The ink-receiving layer in the image-receiving sheet  
is preferably hardened by a curing agent. The curing agent  
is described in Japanese Patent Provisional Publication No.  
H1-161236, pp.222.

15 The layers constituting the image-receiving sheet may  
contain a surface active agent. The surface active agent  
serves as a coating aid, a releasing agent, a slipping  
agent and an anti-static agent. Japanese Patent Provision-  
al Publication Nos. 62-173463 and 62-183457 describe the  
20 surface active agent.

In place of the surface active agent, organic fluorine  
compounds may be used. The organic fluorine compounds  
preferably are hydrophobic. Examples of the compounds in-  
clude fluorine-contained surface active agents, oily  
25 fluorine compounds (e.g., fluorine oil), and solid fluoro-  
carbon resins (e.g. tetrafluoroethylene resin). The or-  
ganic fluorine compounds are described in Japanese Patent  
Publication No. 57-9053 (Column 8-17) and Japanese Patent  
Provisional Publication Nos. 61-20994 and 62-135826.

30 The layers (including a back coating layer) of the im-  
age-receiving sheet may contain a polymer latex. The po-  
lymer latex improves characteristics of the layers. For  
example, it gives dimensional stability, and inhibits curl-  
ing, adhesion, and cracking of the layers. Japanese Patent  
35 Provisional Publication Nos. 62-245258, 62-1316648, and 62-

110066 describe the polymer latex. A polymer latex having a low glass transition temperature (not higher than 40°C) can prevent the layer containing a mordant from cracking and curling. On the other hand, a polymer latex having a  
5 high glass transition point can prevent the back coating layer from curling.

An anti-fading agent may be contained in the layers of the image-receiving sheet. The "anti-fading agent" include anti-oxidizing agent, UV absorber and metal complexes. Ja-  
10 panese Patent Provisional Publication No. H1-161236, pp. 225-247 describes the anti-fading agent.

The image-receiving sheet may contain a fluorescent whitening dye. The whitening dye may be added in the ink.

A particularly preferred support of the image-  
15 receiving sheet is a plastic film or a sheet of paper having surfaces laminated with a film of polyolefin (e.g., polyethylene, polystyrene, polyethylene terephthalate, polybutene, and copolymers thereof). Preferably, a white pigment (e.g., titanium oxide, zinc oxide) or a coloring  
20 dye (e.g., cobalt blue, ultramarine, neodymium oxide) is added into the polyolefin.

Generally, the ink-jet recording method is performed in an on-demand system or in a continuous system. As the head for ink-jet recording (i.e., jet head), bubble jet  
25 type, thermal jet type, and ultrasonic type are known.

There are some types of the ink-jet recording method. For example, in one type, many small drops of thin ink (which is often referred to as "photo-ink") are jetted out. In another type, two or more inks having the same hue but  
30 different concentrations are employed so as to improve image quality. Further, colorless and transparent ink can be used for the ink-jet recording. The present invention is particularly effective in the ink-jet recording method in which many small drops of thin ink are jetted out to print  
35 a photographic image in a high speed.

[Examples]

(Preparation of aqueous ink)

The following components were mixed and stirred for 5 one hour, while the mixture was heated at 30°C to 40°C. The resultant liquid was filtered under pressure through a micro-filter (average pore size: 0.8  $\mu$ m, diameter: 47 mm) to prepare ink A.

10 (Ink A)

	Dye F	4 weight parts
	Diethylene glycol	9 weight parts
	Tetraethylene glycol monobutyl ether	9 weight parts
	Glycerol	7 weight parts
15	Diethanolamine	1 weight part
	Water	70 weight parts

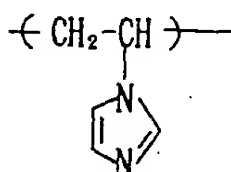
The procedure for preparing the ink A was repeated, except that the dye, the amount of the glycerol, and the 20 polymer according to the invention were changed as is set forth in Table 1. Thus, inks B to Q were prepared.

TABLE 1

Ink	Dye	Polymer and amount thereof	Amount of glycerol	Viscos- ity (cp)	Remark
A	F	-	7	5	Reference
B	B-28	-	7	5	Reference
C	C-7	-	7	5	Reference
D	D-21	-	7	5	Reference
E	E-47	-	7	5	Reference
F	B-28	①10 weight parts	3	5	Invention
G	C-7	①10 weight parts	3	5	Invention
H	D-21	①10 weight parts	3	5	Invention
I	E-47	①10 weight parts	3	5	Invention
J	B-28	②10 weight parts	5	6	Invention
K	C-7	②10 weight parts	5	6	Invention
L	D-21	②10 weight parts	5	6	Invention
M	E-47	②10 weight parts	5	6	Invention
N	B-28	③10 weight parts	2	6	Invention
O	C-7	③10 weight parts	2	6	Invention
P	D-21	③10 weight parts	2	6	Invention
Q	E-47	③10 weight parts	2	6	Invention

Polymer ① of the present invention

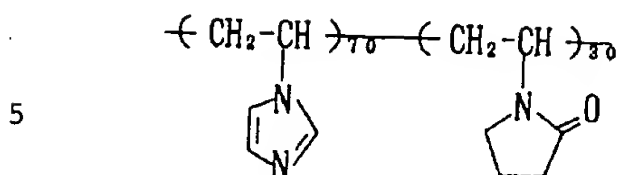
5



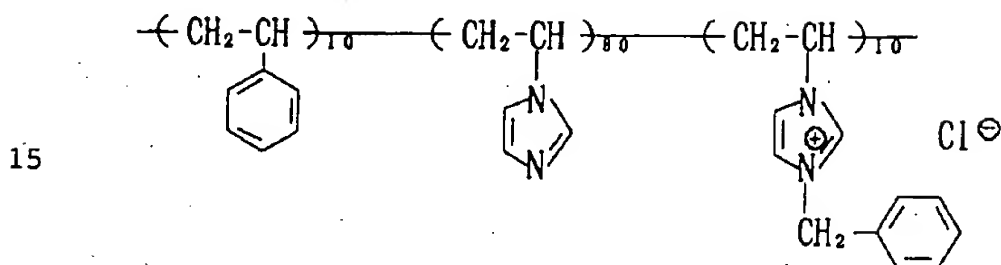
10

Average molecular weight: 15,000

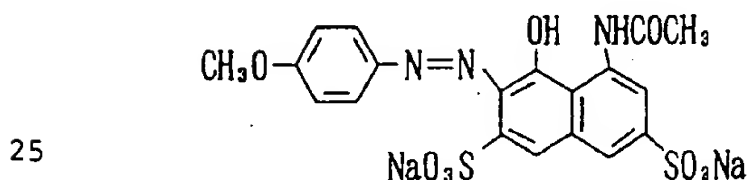
Polymer ② of the present invention



10 Polymer ③ of the present invention



20 Dye F



(Recording and evaluation of image)

30 Using the prepared ink A to Q, an image was printed on a photo-gloss paper sheet [Ink-jet paper (super photo grade), Fuji Photo Film Co., Ltd.] and a super-fine gloss paper sheet (MJA4S3P, Seiko-Epson Co., Ltd., by means of an ink-jet printer [PM-700C, Seiko-Epson Co., Ltd].

Each printed image was evaluated from the viewpoints of hue and resistance against light.

In consideration of the fact that an absorption having a sharp peak gives a clear hue, the image was subjected to  
5 measurement for reflection spectrum using a spectrophotometer and evaluated by the following criteria: A (half width: less than 80 nm), B (half width: 80 - 100 nm), C (too broad to be measured).

The resistance against light was estimated in the following manner. The sample image was exposed to xenon light  
10 (85,000 Lux) by means of a weather meter [Atlas C, 165] for 3 days, and then the image density was measured by means of a reflection densitometer [X-Rite 310TR] for estimating a residual amount of the dye. The dye residual amount was  
15 classified by the following criteria:

A (residual amount: more than 80%), B (residual amount: 60 - 80%), C (residual amount: less than 60%).

The results are set forth in Table 2.

TABLE 2

Ink	Photo-gloss paper		Super-fine gloss paper	
	Hue	Resistance	Hue	Resistance
A	B	A-B	B-C	B-C
B	A	A-B	B	C
C	A-B	A-B	C	C
D	A	A-B	B	C
E	A-B	A-B	C	C
F	A	A	A	A-B
G	A-B	A	A-B	A-B
H	A	A	A	A-B
I	A-B	A	A-B	A-B
J	A	A	A	A-B
K	A-B	A	A-B	A-B
L	A	A	A	A-B
M	A-B	A	A-B	A-B
N	A	A-B	A	B
O	A-B	A-B	A-B	B
P	A	A-B	A	B
Q	A-B	A-B	A-B	B

As is clear from the results, the jet-printing ink of the invention gives an image of good hue and high resistance to light in various receiving sheets.

Further, the images formed of the inks of invention showed less blotting, and had good resistance in water.

#### 10 [Effect of invention]

An image improved in resistance to light and also improved in hue can be formed by using the ink according to



the present invention without depending on the image-receiving sheet on which the image is formed.

[Name of document] Abstract

[Abstract]

[Object] Jet printing ink or ink jet recording method,  
which can form an image improved in hue and resistance to  
5 light without depending on an image-receiving sheet.

[Means] A jet printing ink comprising a dye and an aque-  
ous medium, which further comprises a polymer having a ter-  
tiary amino group or a nitrogen atom-containing heterocyc-  
10 lic group is used in an ink jet recording method.

[Designation of Drawings] None